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Sandia National Laboratories
Waste Isolation Pilot Plant (WIPP)
Test Plan, TP 02-02

**Effects of the MgO Engineered Barrier on the Possible Presence of Mg-Bearing
Colloids and Humic Acids in WIPP**

Revision 1

Task 1.3.5.4.1.2

Effective Date: 11/07/02

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1. Approval Page

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3. List of Acronyms

| | |
|-------------|---|
| ξ | zeta potential |
| κ | Debye-Hückel parameter |
| γ | solution activity coefficient |
| AFM | atomic force microscope |
| a_{H^+} | proton H^+ activity |
| CO_2 | carbon dioxide |
| DI water | deionized water |
| DLVO theory | theory named after Deryaguin, Landau, Verwey and Overbeek |
| HA | humic acids |
| HEPES | N-(2-hydroxyethyl)piperazine-N'-(-2-ethanesulfonic acid) |
| I | ionic strength |
| ICP-OES | induced coupled plasma optical emission spectrometer |
| IEP | isoelectric point |
| kD | kilo Dalton (1 kD = 1 NMWL (i.e. nominal molecular weight limit)) |
| KHP | potassium hydrogen phthalate |
| MES | 2-(N-morpholino)ethanesulfonic acid |
| $MgCO_3$ | magnesite |
| MgO | magnesium oxide |
| MgOH | brucite |
| μm | micrometer |
| nm | nanometer |
| NMWL | nominal molecular weight limit |
| PA | Performance assessment |
| pCH | $-\log[H^+]$ |
| pHr | pH meter reading |
| P_{CO_2} | CO_2 partial pressure |
| PZC | point of zero charge |
| Rev | revision |
| SEM | scanning electron microscope |
| SNL | Sandia National Laboratories |
| T | temperature |
| TOC | total organic carbon |
| TRU | transuranic |
| UF | ultrafiltration |
| US DOE | United States Department of Energy |
| US EPA | United States Environmental Protection Agency |
| UV-vis | ultraviolet-visible |
| V_T | total potential energy of interaction |
| WIPP | Waste Isolation Pilot Plant |

4. Revision History

This is the first revision of this test plan. The original title of TP 02-02, Rev. 0, was “Generation of Colloids from the WIPP Backfill”. The former title has been changed in this revision to capture the nature of the work more accurately. Two tasks are included in TP 02-02, Rev 1: Task 1 (on colloids issued from WIPP backfill) was part of TP 02-02, Rev 0 and Task 2 (on the behavior of humic acids, HA, in the WIPP environment) was part of TP 00-07, Rev 1, “Experimental Study of WIPP MgO backfill at Sandia National Laboratories Carlsbad Facility”. Subsequent revisions of the test plan TP02-02 will be made in accordance with the Sandia National Laboratories Nuclear Waste Management Program Procedures: NP 20-1 Test Plans, NP 6-1 Document Review Process and NP 6-2 Document Control Process.

5. Purpose and Scope

This document describes experiments to study the generation and persistence of colloids under expected WIPP conditions. Colloids may be important to WIPP performance assessment (PA) because of their very large surface areas, mobility, and their ability to bind cations.

- We will evaluate whether MgO, which is being used as an engineered barrier in the WIPP to mitigate the effect of microbial CO₂ generation on actinide mobility in the post-closure repository environment, will generate colloids and whether these colloids will be stable under WIPP conditions.
- HA are products of the biodegradation of animals and vegetal materials; in the case of WIPP, HA may be generated from the degradation of organic materials present in the TRU wastes (cellulosics, plastics, and rubbers). In this task, we will determine the solubility of HA in the presence of MgO in brines representative of the WIPP environment.

6. Background

6.1. Generalities about Colloids

A colloidal phase is an intermediate state between a solution containing dissolved entities of ionic or molecular dimensions, and a solution containing suspended particles sufficiently large to settle by gravity. The size range of colloids is from 1 nm to 1 μ m (Figure 1).

Colloids can be generated by dispersion or condensation. In case of dispersion, material breaks down to colloidal dimensions by some mechanical process (e.g., grinding), or very

high frequency sound waves (ultrasonication) in a liquid-liquid dispersion. Condensation includes dissolution and reprecipitation, condensation from vapor through formation of a mist or fog from a supersaturated vapor, or chemical reactions, including reduction, oxidation or decomposition.

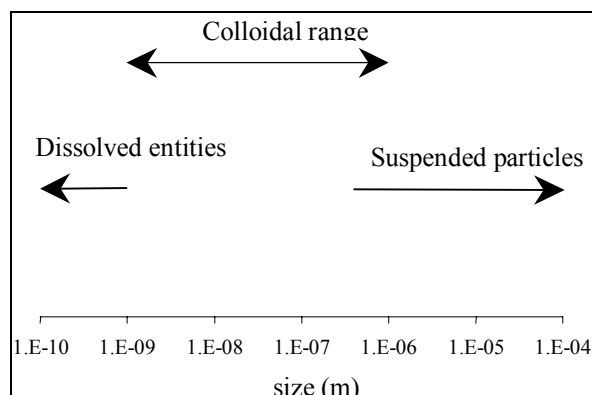


Figure 1. Size ranges of aqueous particles. (Adapted from Gaffney et al., 1996).

Colloids may be important to WIPP PA because they have very large surface areas and may be mobile in aqueous solutions. Additionally, some colloids can retain cations. For example, magnesite (MgCO_3) retains cations such as Co^{2+} , Zn^{2+} , Cs^+ , Ba^{2+} (Shahwan et al., 1998; Erten and Gokmenoglu, 1994); HA form complexes with metals, such as Cr, Cu, Zn, Sr, Cd, Pb (Benes and Mizera, 1996; Esteves Da Silva et al., 1997; Fukushima et al., 1995; Hamilton-Taylor et al., 1997; Samadfam et al., 1996) and in particular with actinides such as Th, U, Np, Am, Cm (Choppin, 1988; Nash and Choppin, 1980; Labonne-Wall et al., 1999; Seibert et al., 2001; Wall et al., 2002; Kim et al., 1991). Consequently, colloids from the WIPP backfill and HA could increase the solubilities of actinides.

6.2. Colloidal Coagulation/Stability

6.2.1. Generalities (Hunter 1993)

Colloids would affect actinide mobility only if they remain as stable suspended entities; coagulated colloids are not mobile. Therefore, it is important to understand the processes leading to stable colloids versus coagulated entities.

The DLVO theory (named after the four scientists Deryaguin, Landau, Verwey and Overbeek) explains the colloidal stability in terms of forces: a repulsive one due to formation of a double layer and an attractive one due to van der Waals interactions. Colloids can possess high negative charges at their surface. As a result, dissolved ions present are retained in a compact layer adjacent to the colloid (i.e., the Stern layer) and a diffuse double layer adjacent to this compact layer. The diffuse double layer contains a

gradually decreasing ionic concentration with increased distance from the colloid surface. When double layered systems interact with each other due to random Brownian motion, the sum of the interactions taking place in the immediate vicinity of the colloid creates a total potential energy of interaction V_T , which defines an energy barrier. V_T is the sum of interactions and repulsions. The stability of a system depends on the height and thickness of the energy barrier. If the potential energy barrier is higher than the thermal energy of the colloidal particles, coagulation is hindered. As the potential energy barrier approaches the thermal energy level, coagulation is increasingly favored. Although the DLVO theory is incomplete (Manciu and Ruckensein, 2001), it has the advantage of simplicity and offers a reasonable approach for obtaining quantitative results.

V_T depends on many parameters that will eventually affect the stability and coagulation of the colloidal population: the temperature T , the charge z of the ion present in the double layer, the double layer thickness $1/\kappa$, in which κ is the Debye-Hückel parameter and is directly proportional to the square root of the ionic strength I . For example, coagulation can result from increasing the ionic strength of the system or increasing the charge density of the neighboring ions.

The colloidal stability will also depend on the degree of ionization of the colloidal surface, which itself is a function of pH. The electrical potential between the bulk solution and the colloid is called zeta potential (ξ); this potential indicates the stability of the colloidal system: the greater ξ (positive or negative), the greater the colloidal stability, as illustrated on Figure 2.

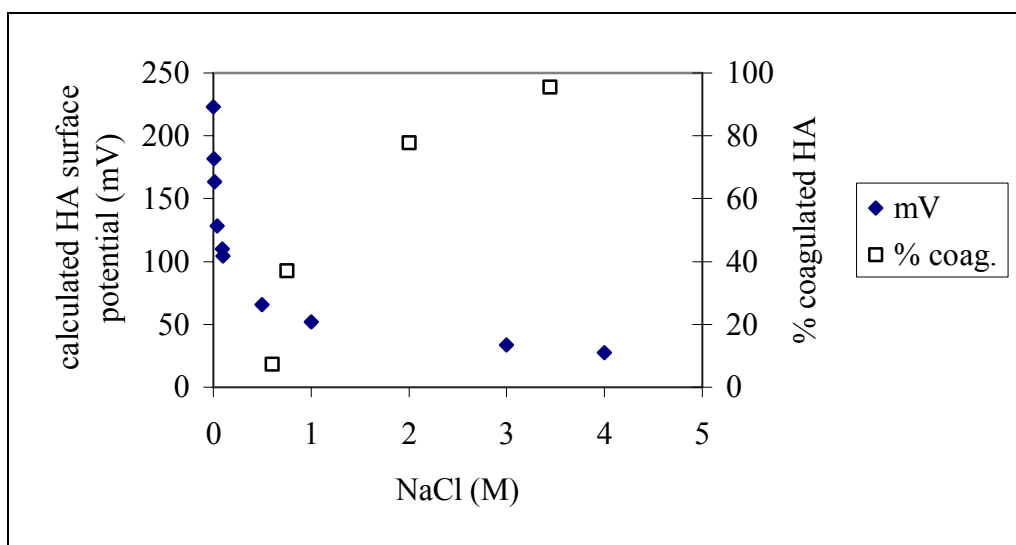


Figure 2. Surface potential and coagulation of humic acids in NaCl solutions, pH 7.5 (adapted from Tombacz and Meleg, 1990).

The isoelectric point (IEP) or point of zero charge (PZC) represents the value of pH at which the colloid has a zero net charge ($\xi = 0$), i.e., the least colloidal stability. For hydroxo complexes $M^{z+}(OH)_n^{z-n}$, the PZC is the pH resulting in an electrically equivalent concentrations of positive and negative complexes. Examples of PZC values for MgO and $Mg(OH)_2$, and HA are presented in Table 1.

Table 1. Examples of PZC values.

| Material | PZC | Ref. |
|-------------------------|----------------|-------------------------|
| MgO | 12.4 ± 0.3 | Parks, 1965 |
| $Mg(OH)_2$ | ≈ 12 | Parks, 1965 |
| HA in 10^{-3} M NaCl | < 2 | Tombacz and Meleg, 1990 |
| HA in 0.1 M NaCl | < 2.5 | Tombacz and Meleg, 1990 |
| HA in 0.5 M to 3 M NaCl | < 3 | Tombacz and Meleg, 1990 |

6.2.2. The particular case of WIPP

The pcH values (i.e., $-\log[H^+]$) of WIPP brines after equilibration with MgO were calculated (US EPA 1998) for the different magnesium carbonate phases expected in the repository; these pcH values are presented in Table 2. Comparison between Tables 1 and 2 show that the estimated WIPP brine pcH values are within the region of colloidal stability for MgO, $Mg(OH)_2$, and HA colloids; unfortunately no PZC values were found in the literature for hydromagnesite, magnesite or nesquehonite.

Table 2. Effects of different magnesium carbonate equilibria with brucite on solution conditions predicted by the FMT model (version 2.2 of FMT, updated version created by SNL in April, 1997, after the CCA).

| Salado Brine | | | | |
|--|-----------------------------|-----------------------------|---------------------------|------------------------|
| | Hydromagnesite ^a | Hydromagnesite ^b | Nesquehonite ^c | Magnesite ^d |
| pcH | 9.13 | 9.37 | 9.36 | 9.31 |
| Log[CO _{2(g)}] | -5.31 | -5.39 | -3.84 | -6.89 |
| Castile Brine | | | | |
| | Hydromagnesite ^a | Hydromagnesite ^b | | |
| pcH | 9.9 | 9.89 | | |
| Log[CO _{2(g)}] | -5.5 | -5.39 | | |
| Hydromagnesite ^a - Mg ₅ (CO ₃) ₄ (OH) ₂ ·4H ₂ O | | | | |
| Hydromagnesite ^b - Mg ₄ (CO ₃) ₃ (OH) ₂ ·3H ₂ O | | | | |
| Nesquehonite ^c - MgCO ₃ ·3H ₂ O | | | | |
| Magnesite ^d - MgCO ₃ | | | | |

Dr. Bernhard Kienzler, from Forschungszentrum Karlsruhe in Germany, has communicated to the author of this document unpublished results regarding the finding of stable colloids originating from brucite. Dr. Kienzler stated: "Literature concerning existence, stability and mobility of colloids in highly concentrated salt solutions is rarely available. In our institute we did some work, however, it is not yet published. In German salt domes Mg bearing salts are available to a large extent, resulting in highly concentrated brines (Q-brine: ~4 m MgCl₂). The brines have a high buffer capacity with respect to pH. In the presence of cement, pH is buffered by precipitation of brucite (Mg(OH)₂) or various magnesium oxychloride hydrates. These phases are not crystalline and show a slow flocculation. We consider the possibility that colloidal phases may be formed even in highly concentrated solutions" (Kienzler, 2001). Moreover, Kienzler has also mentioned that the colloids observed were slow to form (months) and very small at first, consequently difficult to observe.

The experiments planned in this test plan will help determine the concentration of stable colloids generated from MgO under expected WIPP conditions.

It would be difficult to predict the concentration of colloidal HA present in WIPP brines, because HA formation is a slow process; the rate of dissolved HA accumulation reaches an equilibrium in periods of time that vary from 110 years in fine-grained soils to 1500 years in sandy soils (Stevenson, 1994, p. 8). HA coagulation is an easier process to

study. Some studies of HA coagulation under WIPP conditions have been performed at Florida State University (Wall and Choppin, 2000).

Solutions of known ionic strength, pH, Mg, and Ca concentrations were prepared with HA and filtered to obtain the fraction smaller than 100 kD. Over a 50-day period, samples of these solutions were filtered again through 100 kD membranes and the total organic carbon (TOC) of the filtered solutions measured (HA is c.a. 50 wt % TOC). Coagulation occurs in both the absence and presence of light. HA coagulation increases with NaCl concentration. Coagulation also increases in the presence of divalent cations such as Ca^{2+} and Mg^{2+} , but in high ionic strength solutions, neither the Ca^{2+} nor the Mg^{2+} concentrations representative of WIPP brines are sufficient to fully coagulate HA (see Figure 3 and Table 3).

Table 3. Ca^{2+} and Mg^{2+} concentrations in WIPP brines. (Brush, 1990)

| | G Seep | Brine A | ERDA 6 |
|------------------|--------------------------------|------------------------------|------------------------------|
| Ca^{2+} | $7.68 \cdot 10^{-3} \text{ M}$ | $20 \cdot 10^{-3} \text{ M}$ | $12 \cdot 10^{-3} \text{ M}$ |
| Mg^{2+} | 0.630 M | 1.44 M | $19 \cdot 10^{-3} \text{ M}$ |

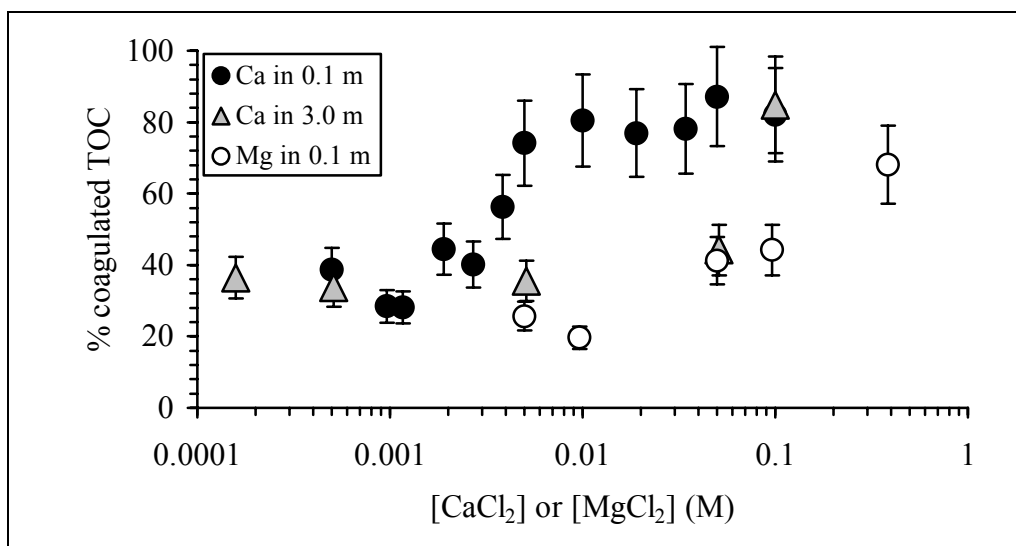


Figure 3. HA (initial TOC = 40 ppm, i.e. HA c.a. 80 ppm) coagulation in NaCl media in presence of varying concentration of CaCl_2 or MgCl_2 , at pH 8.3, after 50 days of equilibration.

No experiments were performed to study HA coagulation in the presence of MgO and at very high ionic strength (5 m). This document is a plan for such experiments.

7. Experiments

7.1. Taks1: Colloids generated from WIPP backfill

7.1.1. Materials

Experiments will be conducted on two MgO samples: pure MgO (Fisher chemicals) and Premier Chemicals MgO. The latter is used as the WIPP engineered barrier. The Premier Chemicals MgO contains impurities such as forsterite $[\text{Mg}_2\text{SiO}_4]$, monticellite $[\text{MgCaSiO}_4]$, and portlandite $[\text{Ca}(\text{OH})_2]$.

MgO suspensions will be prepared in different solutions:

- de-ionized water
- NaCl of different ionic strengths (10^{-3} m to 5 m)
- synthetic WIPP brines prepared in our laboratory:
 - Generic Weep Brine (GWB), which simulates intergranular fluids from the Salado Formation,
 - ERDA-6, which simulate fluids from brine reservoirs in the Castile Formation.

The compositions of GWB and ERDA-6 are presented in Table 4.

Table 4. WIPP Brine Compositions (Brush, 1990)

| | GWB (Salado) | ERDA-6(Castile) |
|----------------------|--------------|-----------------|
| B (mM) | 78 | 63 |
| Br (mM) | 27 | 11 |
| Ca (mM) | 14 | 12 |
| Cl (M) | 5.609 | 4.8 |
| K (mM) | 467 | 97 |
| Mg (M) | 1.018 | 0.019 |
| Na (M) | 3.536 | 4.87 |
| SO ₄ (mM) | 178 | 170 |
| pH | NA | 6.17 |

Different liquid:solid ratios will be applied: 1 g:g – 100 g:g. A variation of the liquid:solid ratio will allow the extrapolation of the results to conditions representative of WIPP. A realistic liquid:solid ratio for WIPP is 0.72 g:g, but the solution analysis of such a sample would be difficult due to the small liquid sample size.

7.1.2. Agitation, Time

The samples will be vigorously shaken while others will be left undisturbed. The shaking motion should accelerate the colloidal process of formation and/or coagulation. The kinetics of the system will be studied by sampling at regular time intervals.

7.1.3. Atmospheric Control

It was estimated in the PAVT (PA Verification Test; Novak, 1997) that the CO₂ fugacity in WIPP would equilibrate at $10^{-5.5}$ (Novak, 1997), while the total gas pressure would range from 30 to 150 MPa (Helton et al., 2000). In WIPP, MgO is expected to convert to hydromagnesite (US EPA, 1998), but experiments presently performed (Wang et al., 2002) show that carbonation of brucite is very slow, even under atmospheric conditions of CO_{2(g)} (fugacity ca. $10^{-3.5}$). To accelerate the conversion process, experiments are also performed in a glovebox containing 5% CO₂ (fugacity ca. $10^{-1.3}$) (Snider and Xiong, 2002).

The first set of colloid experiments will be performed under atmospheric conditions of CO_{2(g)}. Then, the experiments will be conducted in a glovebox, under 5% CO₂, in which conditions the conversion product of MgO and the rate of conversion will be known from the experiments of Snider and Xiong, (2002).

A gas cylinder will provide CO₂ to an airtight glovebox and P_{CO₂} will be monitored with a Bacharach CO₂ analyzer; this instrument monitors CO₂ concentration up to 60%. Additional supply of CO₂ may sometimes be needed to avoid drastic changes of CO₂ pressure in the glovebox after opening the glovebox for sampling. Reaction of sodium bicarbonate with sulfuric acid will provide the needed infusion of CO₂ in the glovebox.

7.1.4. Colloid concentration determination

The supernatant of the solutions will be filtered through filtration membranes, which retains particles larger than 1 μm, the largest colloidal size (e.g. Whatman Nuclepore Track-Etch Membranes). The Mg colloids that would be present in the filtered solutions will be dissolved by adding nitric acid and the Mg concentration (from colloids and soluble species) will be determined with a Perkin-Elmer induced coupled plasma optical emission spectrometer (ICP-OES). Before each daily analysis, the instrument will be calibrated using Mg standards solutions, containing a matrix identical to that of the samples to be analyzed. To correct for drift, an internal standard (e.g., Sc) will be added to the samples and the calibration standard solutions.

A preliminary study was performed to verify the validity of the technique. Variable amounts of MgO (Fisher and Fisher that was previously ground) were stirred in water and nitric acid was added to the samples to obtain a final concentration of 3% HNO₃. The Mg concentration of the samples was measured with the ICP-OES. Figure 4 shows the results of this test.

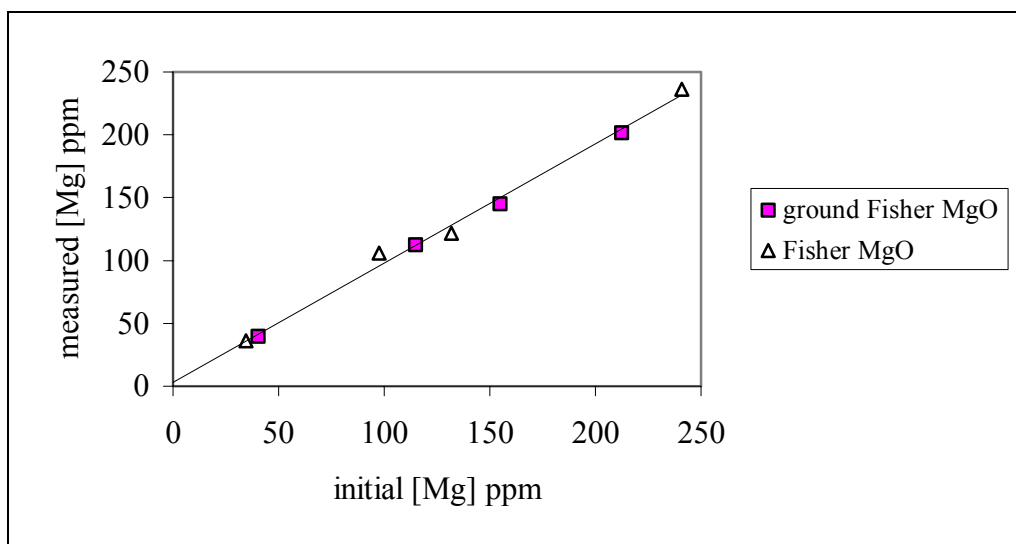


Figure 4. Method development for MgO colloid detection.

$$[\text{Mg}]_{\text{measured}} = 0.950 (\pm 0.024) \times [\text{Mg}]_{\text{initial}} + 2.9 (\pm 3.3), R^2 = 0.996$$

Aliquots of the μm fraction (i.e., fraction of size larger than 1 μm) will be filtered on Millipore/Amicon UF (i.e. ultra-filtration) membrane 1kD, using a pressurized AMICON ultra-filtration cell. 1 kD (kilo Dalton) is equivalent to 1000 NMWL (nominal molecular weight limit). Although there is not a one-to-one relationship of NMWL or cut-off rating of UF membranes to their pore size, an estimation of the membrane pore size was given by Millipore technical assistance to the author of this document: a 1 kD UF membrane presents a pore size of c.a. 1.3 nm, which is the limit between colloids and soluble species. The 1 kD-filtered sample will be acidified with nitric acid and the Mg concentration (representing the soluble Mg species present in the original sample) will be measured by ICP OES. The difference between the Mg concentrations of the 1- μm -filtered samples and the 1-kD-filtered samples will provide the Mg concentration due to Mg colloids.

If colloids are detected, we will study their stability by measuring their zeta potential ξ for the different systems considered, using a Coulter Delsa 440 zeta potential sizer. We will follow the specific procedure for the calibration, use, and maintenance of this instrument (SP 12-3, Rev 0).

7.1.5. pH Control

We will not study the influence of pcH (i.e., $-\log[H^+]$) on the stability of MgO colloids. Biological buffers, such as MES (2-(N-morpholino)ethanesulfonic acid, pKa 6.1) or HEPES (N-(2-hydroxyethyl)piperazine-N'-(-2-ethanesulfonic acid), pKa 7.5) can be used to avoid cation complexation, but they will not buffer MgO suspensions with liquid:solid ratios less than 10^4 g:g. The hydrogen-ion concentration, $[H^+]$, will be measured and expressed as the negative log of the concentration, pcH, rather than using the pH meter reading pH_r, i.e. $-\log a_{H^+}$, in which a_{H^+} is the proton activity; the product of the proton concentration $[H^+]$ and the solution activity coefficient γ . Although pH reference solutions (e.g., Fisher certified color-coded pH buffers, pH 4, 7 or 10) are used for glass electrode calibration in dilute solutions, their use for concentrated solutions is limited because of the significant difference of activity coefficients and liquid-junction potentials between the reference solutions and the solutions to be tested (Chen et al., 1996). To determine the pcH of solutions of high ionic strength, the pH electrode is calibrated daily by titration at fixed ionic strength (NaCl, 0 to 5 *m*). The solutions used for the titration are 0.1 M NaOH, which is prepared weekly from a saturated NaOH solution and standardized with potassium hydrogen phthalate (KHP) and a 0.1 M HCl solution, which is standardized with KHP and the standardized NaOH solutions. At each ionic strength, the equation relating pcH (calculated $-\log[H^+]$) and the solution potential (in mV) is established. The measured potential of a solution can then be converted to pcH. For example, the equation relating pcH, pH_r and the ionic strength of NaCl solutions is: $pcH - pH_r = 0.2212 \times I_{NaCl} + 0.0881$, in which I_{NaCl} is the concentration of NaCl (*m*) (Wall and Choppin, 2002).

WIPP brines contain a variety of constituents (see Table 4). A specific pcH calibration procedure will be determined for these brines, as sulfates and borates would buffer the pH of the solutions.

7.2. Task 2: HA in WIPP

7.2.1. Materials

Two types of MgO will be studied: pure Fisher MgO and Premier Chemicals MgO. HA will be purchased from Aldrich, but the ash content, an indication of impurities, was found to be 50–60 %, after heating a sample at 500 °C for 5 hours (Wall and Choppin, 2002). Most purification techniques described in the literature (Bertha and Choppin, 1978; Nash and Choppin, 1980; Kim et al., 1989) produce very pure organic matter but are very time consuming; such procedures are used when very small amounts of pure HA are needed. Although our experiments require a reasonably pure product, they will also require large amounts (grams) of HA. Aldrich HA will be successively dissolved in base (1 g HA/L in 10^{-2} M NaOH), precipitated in concentrated HCl, and centrifuged. The isolated precipitate will be freeze-dried using a Labconco FreeZone Freeze Dry System

and the ash content of the dried product measured. Such a process has been reported to give less than 5% ash (Wall and Choppin, 2002).

We will study the influence of different media:

- de-ionized water
- NaCl of different ionic strengths (10^{-3} m to 6 m)
- synthetic WIPP brines prepared in our laboratory:
 - GWB
 - ERDA-6

Stock solutions of purified HA will be prepared by dissolving dry organic matter in NaOH solutions in de-ionized water, NaCl or WIPP brine. The stock solution will be filtered through a 1- μ m-pore membrane. The TOC of the stock solutions will be determined (see below). The filtered stock solution will be refrigerated when not in use, because the HA size does not change at low temperature (Wall and Choppin, 2002). Aliquots of the stock solution will be diluted in the solution of interest and MgO will be added. The initial TOC will vary from few ppm to few hundred ppm HA.

The liquid:solid ratios will vary from 1 g:g to 100 g:g, for the reasons explained in paragraph 7.1.1. The slurry will be filtered through a 1 μ m membrane and the TOC of the filtered solution measured.

7.2.2. Agitation, Time, Light Exposure

The purpose of this task is to study the coagulation/precipitation of humic acids. The samples will be shaken for 1 day to allow homogenization and then they will be left undisturbed throughout the rest of the experiments. The kinetics of the system will be studied by sampling at multiple time intervals. Previous results had shown that the coagulation process is accelerated by light exposure (Wall and Choppin, 2002); therefore, a set of experiments will be permanently exposed to light and another set will be kept dark.

7.2.3. Atmospheric Controls

The first set of experiments will be performed under atmospheric conditions of CO₂. The chemistry of elements such as Ca and Mg, and of HA depend on the CO₂ concentration, so a set of experiments will be conducted in a CO₂-free glovebox, purged with N₂ and monitored with a Bacharach CO₂ analyzer.

7.2.4. TOC Measurements

HA concentrations are traditionally determined by UV-visible spectroscopy or total organic carbon content (i.e. TOC) measurement. UV-vis spectroscopy is inadequate for quantitative analysis of HA of small (nm range) variable sizes (Wall and Choppin, 2002). Problems may arise from analyzing TOC in WIPP brines; for example, material containing Na^+ or K^+ will attack the quartz combustion tube. As a result, TOC measurement is time consuming; HA must be extracted from the matrix, and re-dissolved in very low ionic strength medium.

We will study whether the concentration of large (μm) size HA can be determined accurately using UV-vis spectroscopy. The HA concentration of μm -fractionated HA solutions prepared in DI water will be estimated by UV-vis spectrophotometry and compared to the TOC of these solutions. If spectrophotometry provides accurate results, this technique will be adopted for the analysis of the HA coagulation experiment samples.

The absorbance at 465 nm of the μm -fractionated HA samples will be compared to a calibration curve established by recording the absorbance at 465 nm of unfractionated HA solutions of known concentration; the calibration solutions must be of same pH and medium as the fractionated samples. It is also useful to record the absorbances at 665 nm, as the ratio of the absorbances at 465 nm and 665 nm, referred to as the “E4/E6 ratio,” gives useful information as to the size fluctuation of the humic molecules. Such measurements will be performed in our laboratory using a Cary 300 Conc UV-Visible Spectrophotometer coupled to a personal computer loaded with the Cary Win UV ADL Shell Application software.

The TOC of the μm -fractionated HA samples and the unfractionated HA solutions will be measured with a UIC, Inc., Model CM5014 CO_2 Coulometer, CM5130 Acidification Module and CM5120 Furnace Apparatus (following the procedure SP 12-2, Rev 0). The instrument calibration will be checked with standard solutions of sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$). The samples to be measured will first be acidified to pH of about 4-5 and purged with N_2 to remove traces of inorganic carbon, which would alter the TOC measurements.

7.2.5. pH Control

The pcH of the samples will be monitored, but there will be no experiments explicitly intended to study the effects of pH, for the reasons explained in paragraph 7.1.1.1.5.

7.3. Sample Handling, Storage, and Disposal

Standard procedures for sample identification, handling, storage, shipping, archiving and disposition have been described in Sandia National Laboratories Nuclear Waste

Management Program Procedure NP 13-1. Sample handling will be performed under the guidance of NP 13-1.

Samples will be labeled with unique identification numbers and recorded in laboratory notebooks. Solutions will be handled and stored in accordance with documented procedures.

Samples will be stored in the SNL Carlsbad laboratory in various places depending on the experimental procedure.

Solutions will be disposed of in accordance with standard operating procedures in place at the SNL Carlsbad laboratory.

7.4. Equipment Testing

The equipment used for these experiments will be tested in accordance with the Sandia National Laboratories Nuclear Waste Management Program Procedure NP 12-1, Control of Measuring and Test Equipment, and the specific procedure of each instrument.

8. Data Handling

8.1. Data Processing and Mathematical Models

Data processing may be done by hand calculation with the aid of an electronic calculator, or with a standard spreadsheet program, such as Microsoft Excel, according to the Nuclear Waste Management Program Procedure NP 9-1 (“Analysis”). The experimental results and the calculations generated from these results will be reviewed by technical peers.

8.2. Data Identification and Use

Data amenable to written recording will be inscribed by hand in appropriate laboratory notebooks. Such information includes, but is not limited to:

- reagent and solution preparation procedures and results
- sample preparation procedures
- sample composition and conditions e.g. pH, reagent volume, reagent concentration, temperature
- sample handling
- sample analysis procedures and results

8.3. Data Transfer and Reduction Controls

Typical data transfer is from instrumental output to laboratory notebook and from laboratory notebook to a spreadsheet program, if applicable. Printed copies of instrumental output will be permanently attached to the laboratory notebook within the section dedicated to the pertinent experiment.

8.4. Identification, Segregation, Disposal of Erroneous Data

Data suspected to be erroneous will be tested by comparison to replicate samples or replicate experiments. Statistical justification for rejection of erroneous data will be provided within the laboratory notebook.

9. Training and Other Standard Procedures

All personnel participating in the work described in this Test Plan will be trained and qualified for the assigned tasks. This requirement will be implemented in accordance with NWMP procedure NP 2-1, "Qualification and Training." Evidence of qualification and training will be documented with Form NP 2-1-1, "Qualification and Training."

Additionally, the following NWMP Procedures and Project Specific Procedures are applicable:

SOP-C001: "Standard Operating Procedure for Activities in the SNL/Carlsbad Laboratory Facility."

SP 13-1, "Chain of Custody"

SP 12-3, "Calibration, Use, and Maintenance of the DELSA-440 Electrophoretic Mobility Analyzer"

SP 12-2, "Use and Maintenance of the UIC, Inc. Model CM5014 CO₂ Coulometer, CM5130 Acidification Module and CM5120 Furnace Apparatus"

NP 6-1, "Document Review Process"

NP 9-1, "Analysis"

NP 13-1, "Sample Control"

NP 12-1, "Control of Measuring and Test Equipment"

NP 20-2, "Scientific Notebooks"

NP 2-1, "Qualification and Training"

NP 17-1, "Records"

10. Health & Safety

The health and safety requirements relevant to the tasks for work in this test plan are described in SOP-C001.

11. Permitting/Licensing

There are no special licenses or permitting requirements for the work described in this test plan.

12. References

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